FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF $CaCO_3$ AND CaO

by

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AUTHOR'S DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF $CaCO_3$ AND CaO". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this or any other examining body or university.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
ASTM	American Standard for Testing Materials
BBD	Box-Behnken Design
CA	$CaAl_2O_4$
CA_2	$CaAl_4O_7$
CA_6	$CaAl_{12}O_{19}$
CCD	Central Composite Design
CTE	Coefficients of Thermal Expansion
DF	Degree of Freedom
DM	Dolehert Matrix
DOE	Design of Experiment
EDX	Energy Dispersive X-ray
F-test	Fisher test
FCC	Face Centred Cube
FESEM	Field Emission Scanning Electron Microscope
FT	Fracture Toughness Model
GFD	General Factorial Design
GOF	Goodness of Fit
GPa	Giga Pascal
HIP	Hot Isostatic Pressing
HV	Vickers hardness
kgf	Kilogram-force

ICDD	International Centre for Diffraction Data
ISO	International Standard Organization
LOF	Lack of Fit
MLR	Multiple Linear Regression
MOR	Modulus of Rupture
MPa	Mega Pascal
MR	Multiple regression
m-ZrO2	Monoclinic Zirconia
RSM	Response Surface Methodology
SEM	Scanning Microscope Electron
t-ZrO2	Tetragonal Zirconia
wt.%	Weight percentage
XRD	X-ray diffraction
YSZ	Yttria Stabilised Zirconia
ZTA	Zirconia Toughened Alumina

LIST OF SYMBOLS

A	Calcination Temperature
a	Half Of The Indentation Diagonal Length
B	Particle Size
b_o	Coefficient Of Intercept
b_i	Coefficient Of Intercept
b_{ii}	Coefficient Of Intercept
b_j	Coefficient Of Intercept
C	Concentration of Reactants
E	Modulus Young
HV	Vickers hardness
K_{1c}	Fracture toughness
k	Number Of Factors
l	Length of the radiant crack
N	Number of Experiments
n	Number of Centre Points
(t)	Tetragonal phase
(m)	Monoclinic phase
X_i	Independent Variable
X_j	Independent variable
Y	Response
α	Rotatability
β	Error Function
ρb	Bulk density

PENINGKATAN KELIATAN PATAH ALUMINA DIPERKUAT ZIRKONIA (ZTA) MELALUI PENAMBAHAN GABUNGAN $CaCO_3$ DAN CaO

ABSTRAK

Alumina yang diperkuat zirkonia (ZTA) merupakan sebatian seramik yang amat berguna dalam teknologi industri masa kini. Walau bagaimanapun, sifat keliatan patah ZTA yang rendah menghadkan penggunaan yang meluas dalam bidang kejuruteraan. Oleh itu, penambahbaikan bagi keliatan patah adalah penting. Oleh yang demikian, kepentingan untuk mengekalkan kekerasan yang tinggi dan meningkatkan keliatan patah akan meningkatkan kebolehpercayaan penggunaan ZTA dalam aplikasi teknologi. Pembentukan *in situ* butiran memanjang $CaAl_{12}O_{19}$ di dalam seramik ZTA ketika proses pensinteran menjadi pilihan. Keadaan ini disebabkan ia lebih mudah disinter, selamat dari bahaya kesihatan dan untuk mengelakkan kaedah pensinteran yang rumit dan kurang ekonomik. Serbuk-serbuk CaO dan $CaCO_3$ telah ditambah ke dalam ZTA, diadun basah, dimampat ekapaksi dan pembentukan ZTA melalui pensinteraan keadaan pepejal tanpa dikenakan tekanan. Kajian ini dibahagikan kepada tiga bahagian. Bahagian pertama ialah penambahan hanya $CaCO_3$ ke dalam ZTA. Keliatan patah meningkat dari 5.95 $MPa.m^{1/2}$ untuk ZTA tulen kepada 6.3 $MPa.m^{1/2}$ untuk ZTA ditambah dengan 0.5 wt.% $CaCO_3$ disebabkan oleh mekanisme pesongan retak di sepanjang butiran $CaAl_{12}O_{19}$. Walau bagaimanapun, nilai kekerasan menurun disebabkan oleh penguraian $CaCO_3$ yang membebaskan CO_2 dan membentuk mikrostruktur berliang. Oleh itu, melalui penambahan gabungan CaO dan $CaCO_3$ ke dalam ZTA untuk mengurangkan keliangan dan serentak dengan itu mendapatkan butir-butir memanjang $CaAl_{12}O_{19}$ yang meningkatkan keliatan patah ZTA melalui mekanisme-mekanisme pesongan retak dan

penyambungan retak. Di dalam bahagian kedua, gabungan penambahan di antara CaO dan $CaCO_3$ telah ditetapkan pada 0.5 wt.%. Kekerasannya telah meningkat dan menghasilkan keliatan patah yang lebih baik disebabkan mikrostuktur ZTA yang kurang berliang dan saiz serta bentuk butir-butir $CaAl_{12}O_{19}$ yang terkawal. Komposisi optimum ZTA ialah dengan gabungan penambahan 0.4 wt.% CaO dan 0.1 wt.% $CaCO_3$. Komposisi ini memberikan keliatan patah maksimum (6.51 $MPa.m^{1/2}$) dan kekerasan yang berpatutan (1592 HV). Oleh itu, nisbah 4:1 untuk CaO:$CaCO_3$ telah dipilih sebagai asas kepada bahagian ketiga eksperimen. Bahagian ketiga ialah kajian mengenai kesan-kesan interaksi bagi tiga parameter, suhu pensinteran, tempoh rendaman dan gabungan di antara CaO dan $CaCO_3$ ke atas pengukuhan keliatan patah dan kekerasan Vickers ZTA. Rekabentuk Eksperimen (DOE) telah dilakukan untuk mengurangkan bilangan ujian dan sementara itu, proses pengoptimuman dijalankan untuk mengoptimumkan julat berkesan setiap respon. Selepas menggunakan Metodologi Permukaan Respon (RSM), adalah dibuktikan bahawa tempoh suhu pensinteran ialah pembolehubah yang paling berpengaruh terhadap keliatan patah dan kekerasan seramik ZTA. Keputusan optimum (keliatan patah ialah 6.84 $MPa.m^{1/2}$ dan kekerasan 1615 HV) diperolehi dari suhu pensinteran pada 1600 °C, gabungan di antara CaO dan $CaCO_3$ 0.95 wt.% dan tempoh rendaman 2.14 jam. Rekabentuk-rekabentuk lain seperti Analisis Varians (ANOVA), kekurangan penyesuaian, pemetaan 3D dan Analisis Baki telah mengesahkan kesesuaian keputusan yang diperolehi. Walau bagaimanapun, pengesahan keputusan yang diperolehi daripada eksperimen-eksperimen menunjukkan bahawa keputusan optimum (keliatan patah ialah 7.1 $MPa.m^{1/2}$ dan kekerasan 1584 HV) yang perolehi daripada 1.05 wt.% gabungan di antara CaO dan $CaCO_3$, suhu pensinteran pada 1600 °C, dan tempoh rendaman 2.9 jam. Nilai-nilai ini adalah standing dengan formula daripada RSM.

FRACTURE TOUGHNESS ENHANCEMENT OF ZIRCONIA TOUGHENED ALUMINA (ZTA) THROUGH ADDITIONS OF COMBINATION OF $CaCO_3$ AND CaO

ABSTRACT

Zirconia Toughened Alumina (ZTA) is a successful ceramic compound in new technological industry. However, its low fracture toughness limited the usage of ZTA in many engineering applications. Therefore, the enhancement of fracture toughness is necessary. Nonetheless, it is crucial to maintain high hardness and enhance the fracture toughness to make ZTA more reliable for technological applications. In-situ formation of elongated $CaAl_{12}O_{19}$ grains inside ZTA ceramics during sintering process is preferred. This is due to its easy to be sintered, safety from health hazards and to avoid more complicated and less economical methods of sintering. CaO and $CaCO_3$ powders were added into ZTA, wet-mixed, uniaxially pressed and ZTA samples formed by pressureless solid state sintering. The current study is divided to three parts. The first part is the addition of $CaCO_3$ alone into ZTA. The fracture toughness was improved from 5.95 MPa.$m^{1/2}$ for pure ZTA to 6.3 MPa.$m^{1/2}$ for ZTA added with 0.5 wt. % of $CaCO_3$ due to crack deflection mechanism along elongated $CaAl_{12}O_{19}$ grains. However, the hardness decreased due to emission of CO_2 which creates porous microstructure. Hence, CaO and $CaCO_3$ added together into ZTA to reduce the porosity and simultaneously, obtain elongated $CaAl_{12}O_{19}$ grains which enhances the fracture toughness of ZTA through crack deflection and crack bridging mechanisms. In the second part, combination addition between CaO with $CaCO_3$ was fixed at 0.5 wt. %. The hardness was improved and better fracture toughness was obtained due to less

porous microstructure of ZTA and control of the size and shape of $CaAl_{12}O_{19}$ grains. The optimum ZTA composition was added with 0.4 wt. % CaO combined with 0.1 wt. % $CaCO_3$. This composition has the maximum fracture toughness (6.51 $MPa.m^{1/2}$) and reasonable hardness (1592 HV). Therefore, the $CaO/CaCO_3$ ratio of 4:1 was selected as the base for the third part. The third part is to study the interaction effects of three parameters: sintering temperature, soaking time and combination addition between CaO and $CaCO_3$ on the two responses: fracture toughness and Vickers hardness of ZTA. The Design of Experiments (DOE) was implemented to reduce the number of tests and meanwhile the optimisation process was employed to optimise the effective range of responses. After applying Response Surface Methodology (RSM), it was proved that sintering temperature is the most influence parameter on the fracture toughness and hardness of ZTA ceramics. The optimum results (fracture toughness of 6.84 $MPa.m^{1/2}$ and hardness 1615 HV) obtained from sintering temperature at 1600 °C, combination addition between CaO and $CaCO_3$ of 0.95 wt.%, and soaking time for 2.14 hr. The other designs such as Analysis of Variance (ANOVA), Lack of Fit (LOF), 3D mapping and Residual Analysis have also confirmed the adequacy of the result. However, confirmation results obtained from experiments found that the optimum results (fracture toughness 7.1 $MPa.m^{1/2}$ and Vickers hardness was 1584 HV) were obtained from 1.05 wt.% of combination addition between CaO and $CaCO_3$ into ZTA samples, sintering temperature of 1600 °C and soaking time of 2.9 hr. These values are comparable with empirical formulas from RSM.

CHAPTER 1

INTRODUCTION

1.1. Research Background

Zirconia Toughened Alumina (ZTA) is an innovative and high performance ceramic compound which combines high strength, moderate toughness with high wear resistance and outstanding hardness (Kern *et al.*, 2015; Naga, Hassan and Awaad, 2015; Pfeifer *et al.*, 2016). Therefore, it is a promising candidate for structural materials such as motor, aerospace, cutting inserts, wear components, biomedical field, , implants, bushings, valve seats, dies, bearings, insulators, refractory uses, high temperature filtering, and armours (Maiti and Sil, 2011; Yao *et al.*, 2015; Xia *et al.*, 2016) It consists of the alumina (Al_2O_3) matrix which provides high strength and hardness and it is embedded with zirconia (ZrO_2) particles which promotes the fracture toughness. ZrO_2 is the intrinsic phase undergoes tetragonal to monoclinic phase transformation. This phase transformation is accompanied by approximately 4-6% volume expansion which causes stress induced transformation toughening and microcrack toughening. Consequently, compressive stress is produced around the crack tips which hampers crack propagation (Maiti and Sil, 2010; Sommer *et al.*, 2012).

ZrO_2 has three polymorphs: monoclinic (m), tetragonal (t) and cubic (c). The phase transformation of pure ZrO_2 is occurred with temperature variation. Hence, the fracture toughness of ZTA is based on this phase transformation (Jin, 2005). However, ZTA fracture toughness is still below the requirement for some engineering applications. Hence, many approaches have been taken to improve the fracture